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Treatability Studies of Pesticide Manufacturing Wastewaters: Dazomet

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16. ABSTRACT The report gives results of laboratory studies of the treatability of manufacturing wastewater from synthesis of the pesticide, dazomet. A tiered approach was taken: the lest costly and most available treatments were investigated first. Effluent from the manufacture of dazomet was tested for treatability by activated sludge systems when diluted to 1:100, 1:500, and 1:1000 in municipal wastewater. At 1:100, dazomet showed greater than 95% reduction after biological treatment; however, effluent COD levels were unacceptably high at an average of 160 mg/liter. At 1:500, effluent COD was much closer to the control effluent; however, nitrification of ammonia was severely hampered. At 1:1000, dazomet wastewater had a variable effect on nitrification while effluent COD levels were close to those of controls. It is recommended that dazomet wastewater be diluted to at least 1:1000 in municipal wastewater to minimize the negative effects on the nitrification of ammonia during the activated sludge treatment process.

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TREATABILITY STUDIES OF PESTICIDE MANUFACTURING WASTEWATERS: DAZOMET

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Task 109

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ABSTRACT

Laboratory studies of the treatability of the manufacturing wastewater due to synthesis of the pesticide Dazomet were undertaken. A tiered approach was taken in which the least costly and most available treatments were investigated first.

The effluent from the manufacture of dazomet was tested for treatability by activated sludge systems when diluted 1:100, 1:500, and 1:1000 in municipal wastewater. At dilutions of 1:100 dazomet concentrations showed greater than 95% reduction after biological treatment. However, effluent COD levels were unacceptably high at an average of 160 mg/L. At 1:500 levels the effluent COD was much closer to the control effluent. However, nitrification of ammonia was severely hampered. At 1:1000 dilutions the dazomet wastewater had a variable effect on nitrification while effluent COD levels were close to controls. It is recommended that dazomet wastewater be diluted to at least 1:1000 in municipal wastewater to minimize the negative effects on the nitrification of ammonia during the activated sludge treatment process.

No difference in toxicity to Daphnia magna or Selenastrum capricornutum was noted in effluents from activated sludge units fed 1:500 or 1:1000 dilutions and units fed municipal wastewaters alone.

Pretreatment of the dazomet wastewater by air stripping under alkaline conditions (pH 11) reduced the dazomet concentrations but had no effect on the COD or ammonia concentration. Air stripping at low pH was not attempted due to the generation of toxic carbon disulfide under these conditions.

This report was submitted in partial fulfillment of Contract No. 68-02-3688 by the Research Triangle Institute under the sponsorship of the U. S. Environmental Protection Agency. This report covers a period from August 1, 1979 to October 31, 1979 and work was completed as of November 15, 1979.

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SECTION 1
INTRODUCTION

In February 1979 Research Triangle Institute (RTI) was requested by the Industrial Environmental Research Laboratory, Research Triangle Park (IERL-RTP) of the U. S. Environmental Protection Agency (EPA) to conduct laboratory and pilot studies of the treatability of pesticides manufacturing wastewaters. The project is designed to investigate the suitability of individual pesticide manufacturing wastewaters for discharge to biological treatment systems, whether publicly owned treatment works (POTW) or on-site systems.

The approach taken with each pesticide manufacturing wastewater is prioritized, that is, less costly, more available methods of treatment are investigated first. The preferred method of treatment is assumed to be biological treatment. If the pesticide is judged suitable to biological treatment, a judgment based on chemical and toxicological evaluation of the waste before and after treatment, additional options are not investigated.

If pesticide manufacturing wastewater disrupts biological treatment systems, the possibility of pretreating the waste prior to biological treatment is investigated. Pretreatment options may include pH adjustments, filtration, flocculation, oxidation and others depending on the nature of the waste and its chemical composition.

If pretreatment does not make the waste compatible with biological treatment, that is, activated sludge systems, adsorption techniques may be investigated. These may include both carbon and resin systems. The efficiency of physical-chemical treatment of wastewaters would then be evaluated as with the biological treatment system.

This report details a study of the treatability of wastestreams from the manufacture of dazomet by Vinings Chemical Company, Marietta, Georgia.

SECTION 2
CONCLUSION AND RECOMMENDATIONS

The effluent from the manufacture of dazomet was tested for treatability by activated sludge systems when diluted 1:100, 1:500, and 1:1000 in municipal wastewater. At 1:100 dilutions dazomet concentrations showed greater than 95% reduction after biological treatment. However, effluent COD levels were unacceptably high at an average of 160 mg/L. At 1:500 levels the effluent COD was much closer to the control effluent. However, nitrification of ammonia was severely hampered. At 1:1000 dilutions the dazomet wastewater had a variable effect on nitrification while effluent COD levels were close to controls. It is recommended that dazomet wastewater be diluted to at least 1:1000 in municipal wastewater to minimize the negative effects on the nitrification of ammonia during the activated sludge treatment process.

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Pretreatment of the dazomet wastewater by air stripping under alkaline conditions (pH 11) reduced the dazomet concentrations but had no effect on the COD or ammonia concentration. Air stripping at low pH was not attempted due to the generation of toxic carbon disulfide under these conditions.

SECTION 3

DAZOMET

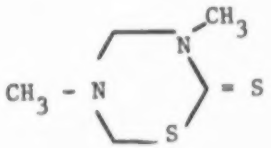
CHEMICAL INFORMATION

Chemical Names: Tetrahydro-3,5-dimethyl-2H-1,3,5-thiadiazine-2-thione; 3,5-Dimethyl-1,3,5-2H-tetrahydrothiadiazine, 2-thione.

CAS No. 533-74-4.

Synonyms: Mylone, Basamid; Crag Fungicide®; Crag Nemacide®; Micro-Fume®; 3,5-D.

Structure:

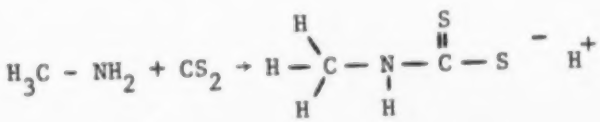


Category: Dithiocarbamate

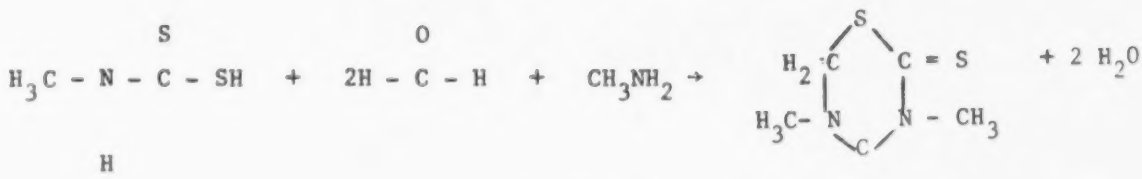
Properties: M.W.-150.27. Forms white almost colorless, crystals at room temperature. Melting point: 105-106°C.

MANUFACTURE

Dazomet is manufactured in a batch production process. The synthesis involves the formation of the dithiocarbamate intermediate by the reaction of carbon disulfide with methylamine:



The dithiocarbamate is then condensed with formaldehyde in presence of additional methylamine to produce dazomet (personal communication, J. Len):



PRESENT WASTEWATER DISPOSAL PRACTICES

Wastewater from the manufacture of dazomet results from the filtration of the final product. This filtrate is combined with washwater from the product rinse step and is stored onsite for contract hauling and land disposal. Wastewater generation occurs at intervals due to the batch process used; a total of 375,000 gallons of wastewater per year is generated.

ECOLOGICAL AND HEALTH EFFECTS

A literature search relative to human health and ecological effects data was conducted via the computer files TOXLINE and BIOSIS. Several hundred references were available, but the vast majority dealt with dazomet's use as a soil sterilant and its effect on soil microorganisms. Data pertaining to dazomet's fate in the soil and its effect on mammalian species are presented below.

FATE IN THE SOILS

The degradation of dazomet is complex in the number and variety of pathways and the reactivity of several of its breakdown products. Figure 1, as adapted from McKenzie (1957), summarizes several possible pathways for its degradation. The numbers in parenthesis in Figure 1 correspond to the description following in the text.

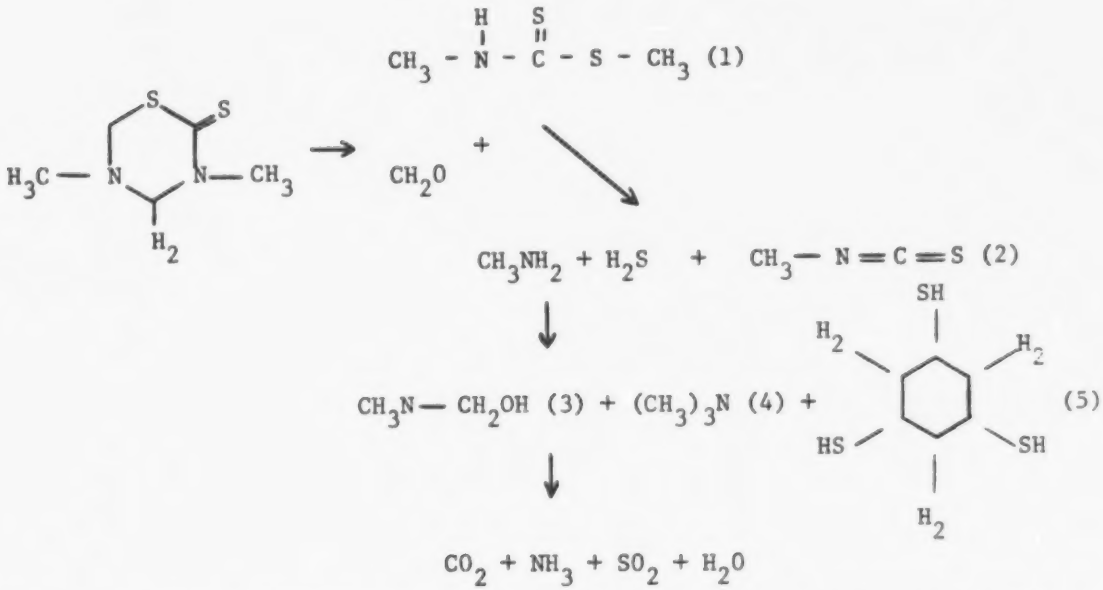


Figure 1. Proposed pathway for the degradation of dazomet (McKenzie, 1957).

A similar description is contained in a product information bulletin which gives the breakdown as follows (Anonymous, 1957). In step 1 dazomet hydrolyzes to form formaldehyde and methylamine methyldithiocarbamate (1). In the second step, (1) breaks down further to form methylamine, hydrogen sulfide and methylisothiocyanate (MIT,2). Methylamine, hydrogen sulfide, and formaldehyde may react to form methylaminomethanol (3), or trimethylamine (4). The amines are said to further react to give $CO_2 + NH_3 + H_2O$. Methylisothiocyanate (2) is unstable in the presence of water and also reacts to give CO_2, H_2S and methylamine. The methyamine reacts further to give CO_2 and NH_3. The 1,3,5-trithiocyclohexane (5) is not mentioned in this description (Anonymous, 1957).

There is some controversy over possible breakdown products of dazomet particularly the form of the dithiocarbamate in step 1 above and the reactions involving MIT (see Goksoyr, 1964). Drescher and Otto (1968) also report isolating a compound which they identified is 1,3,5-trimethylhexahydro-triazine-thione which is postulated be a condensation product of symmetrical dimethyl thiourea, formaldehyde, and methylamine from the degradation of dazomet in soil.

Studies of the fate and mode of action of dazomet have some relevance to the treatment of production wastewaters. The nematicidal and fungicidal effects of dazomet are due apparently to the degradation products of dazomet rather than the parent compound itself. Goksoyr (1964) gave methylisothiocyanate a major role in the fungicidal effect of dazomet though he did not rule out the effect of formaldehyde. Torgeson et al (1957) have stated that MIT, formaldehyde, H_2S, and methylamine are some of the breakdown products of dazomet and claim that the effect of the breakdown products applied to soil singly at concentrations expected from degradation of dazomet is not as great as the effect of the combination of products resulting from the application of dazomet itself. Unfortunately none of the details or methods of their studies are presented. Munnecke et al, (1962) found a close correlation between the production of MIT and the fungicidal effects of dazomet, though their testing methods may have excluded the effect of other less volatile degradation products.

The rate of release of MIT in the use of dazomet has been studied fairly extensively. Munnecke and Martin (1964) found that the rate of release of MIT increased with increasing soil moisture. At 80% of saturation the cumulative MIT production reached a plateau in about 68 hours although MIT production was not stoichiometric with dazomet applied. The release was the same in autoclaved and non-autoclaved soil indicating a non-biological mechanism. Rate of MIT release also increased with increasing temperature and generally with increasing pH up to 7. Despite the greater production of MIT found at higher soil fungicidal effect in soil at 45% water saturation than soil at 70% of saturation. This effect probably reflects the greater diffisivity of MIT in soils at lower water content (Vanachter and Van Assche, 1970).

The half time of MIT in the soil varied greatly with temperature and soil type. At 23°C the value ranged from 4 to 8 days (Smelt and Leistra, 1974). Decomposition of dazomet occurs more rapidly. Drescher and Otto (1968) found that decomposition was complete in as little as 4 hours at 20°C.

Two additional reports have been made of the inhibition of nitrification by dazomet and MIT. Smith and Weeraratna (1975) report that dazomet incorporated in soil at 100 ppm, increased ammonium concentration for 2 weeks after application though the effect was temporary. Tomlinson et al (1966) report that MIT at concentrations of 0.8 mg/ℓ inhibited oxidation of ammonia in activated sludge processes by 75%.

HEALTH EFFECTS

Dazomet has been found to be non-mutagenic in two separate investigations (Rasanen et al., 1977 and Anderson et al. 1972).

Smyth et al (1966) report extensive mammalian toxicological testing of dazomet. Table 1 summarizes some of their findings. Smyth et al (1966) also report that 40 ppm in the diet of rats for a period of two years is the lowest truly injurious levels of dazomet; though some liver and kidney irritation was noted at 10 ppm. 640 ppm in diet of rats for 2 years did not effect mortality but reduced growth and caused liver and kidney lesions. No consistent pattern of tumor formation was noted in dazomet-treated rats.

Ottnad et al (1978) report that the acute oral LD_{50} to rats of MIT is 95-175 mg/kg of body weight. Acute dermal toxicity (LD_{50}) of MIT to rats is 2780 mg/kg and acute intraperitoneal toxicity (LD_{50}) to rats is 49 mg/kg.

TABLE 1. TOXICOLOGICAL DATA FOR DAZOMET

Organism	Route of Application	LD_{50} (g/kg)
Rat	Oral	0.32 to 0.62
Mice	Oral	0.18
Pig	Oral	0.16
Rabbit	Oral	0.12
Rat	Intraperitoneal	0.087
Rabbit	Intraperitoneal	0.127
Dog	Intraperitoneal	0.055

SECTION 4
TREATABILITY STUDIES

CHARACTERIZATION OF WASTEWATER FROM DAZOMET MANUFACTURE

The supernatant remaining after the reaction and precipitation of dazomet and the washwater used in the product purification step are combined in a holding tank for trucking to a land disposal site. Because the wastewater is presently hauled for disposal, water use is minimized at the plant which results in a concentrated wastestream. The wastewater resulting from several production runs was combined in a holding tank and sampled and shipped to RTI.

Analyses by plant personnel of the first sample sent to RTI revealed that this sample had been contamined with wastes from another manufacturing process. At this point a second sample was shipped to RTI after verification of noncontamination. Table 2 provides characterization data on these two samples which indicates their similarity in most parameters with an exception of the methylene bis thiocyanate contained in the contaminated sample.

BIOLOGICAL TREATMENT I

An initial attempt was made to test the biological treatability of dazomet wastewater (Sample 1) by activated sludge units. Two bench scale activated sludge units (see Appendix C) were fed primary settled municipal wastewater spiked 1% with dazomet wastewater and buffered with 0.4 g/L of $NaHCO_3$. Influent samples were mixed daily. Two units were run as controls with buffered municipal wastewater alone. Mixed liquor volatile suspended solids were initially determined to be 3500 and 4100 mg/L in the control units and 3100 and 3800 mg/L in the test units. A sludge age of between 25 and 30 days was maintained with some additional wastage occuring in the units with higher solids levels to maintain a solids level between 2500 and 3500 mg/L. Oxygen levels were maintained at 3.0 mg/L or greater.

TABLE 2. PESTICIDE MANUFACTURING WASTEWATER CHARACTERIZATION.

Parameter	Sample 1	Sample 2
pH	7.7	7.4
Cl^-, mg/L	3710	3280
Alkalinity, mg/L as $CaCO_3$	800 to pH 5.5	2650 to pH 4.4
Total Kjeldahl Nitrogen, mg/L as N	1910	2190
Ammonia, mg/L as N	670	1320
Oxidized Nitrogen, mg/L as N	-	95
Total Phosphorus, mg/L	-	0.66
Chemical Oxygen Demand, mg/L	24,200	20,300
Dazomet, mg/L	3150	2400
Methyl Isothiocyamate, mg/L	200	280
Methylene Bisthiocyanate mg/L	700-800*	None Detected

*Data provided by plant personnel.

Influent chemical oxygen demand of the dazomet feed averaged 467 mg/L as shown in Figure 2, days 4 through 34. Control influent COD averaged 257 mg/L as shown in Figure 3, days 4 through 34.

Test unit effluent COD averaged 164 mg/L which amounts to a 65% reduction. Range of effluent values was 113 to 230 mg/L. Control unit effluent averaged 42 mg/L, which represents a 83% reduction in COD. This reduction in control unit COD is comparable to the reduction achieved across the secondary treatment portion of a full scale biological treatment plant.

After thirty days of testing it was apparent that the high influent COD of the test units prevented a reduction comparable to control units. In addition, dazomet wastewater at this concentration also interferred with nitrification in the test units. Ammonia levels in the test units influent averaged 34 mg/L as N and the effluent averaged 30 mg/L as N. Comparable values for control units were 24 and < 0.5 mg/L as N.

A positive result was noted in the pesticide reduction across the test activated sludge units. Considerable reduction in dazomet concentration also occurred during the 24 hour shelf life of the combined dazomet municipal wastewater. Freshly mixed wastewater showed a dazomet concentration of 19.6 mg/L. The concentration of solutions which were refrigerated (4°C) for 18 hours showed a dazomet concentration of 19.4 mg/L while dazomet concentrations in solutions which sat a room temperature for 18 hours were reduced to concentrations of 11.1 to 13.1 mg/L. A solution which was refrigerated for 24 hours and which sat at room temperature for an additional 24 hours showed a reduction of dazomet to 8.1 mg/L. Effluent from test units analyzed during the first week contained 3.3 and 2.0 mg/L dazomet. Effluents analyzed from the fourth week of operation contained < 1 mg/L dazomet. As noted in the literature review, the instability of dazomet particularly in the presence of water is a positive sign for degradation during biological treatment though consideration must be given to the toxicological properties of the degradation products.

PRETREATMENT OF DAZOMET WASTEWATER

While the pesticide showed ready decomposition, it was apparant that successful treatment would require either additional dilution or a

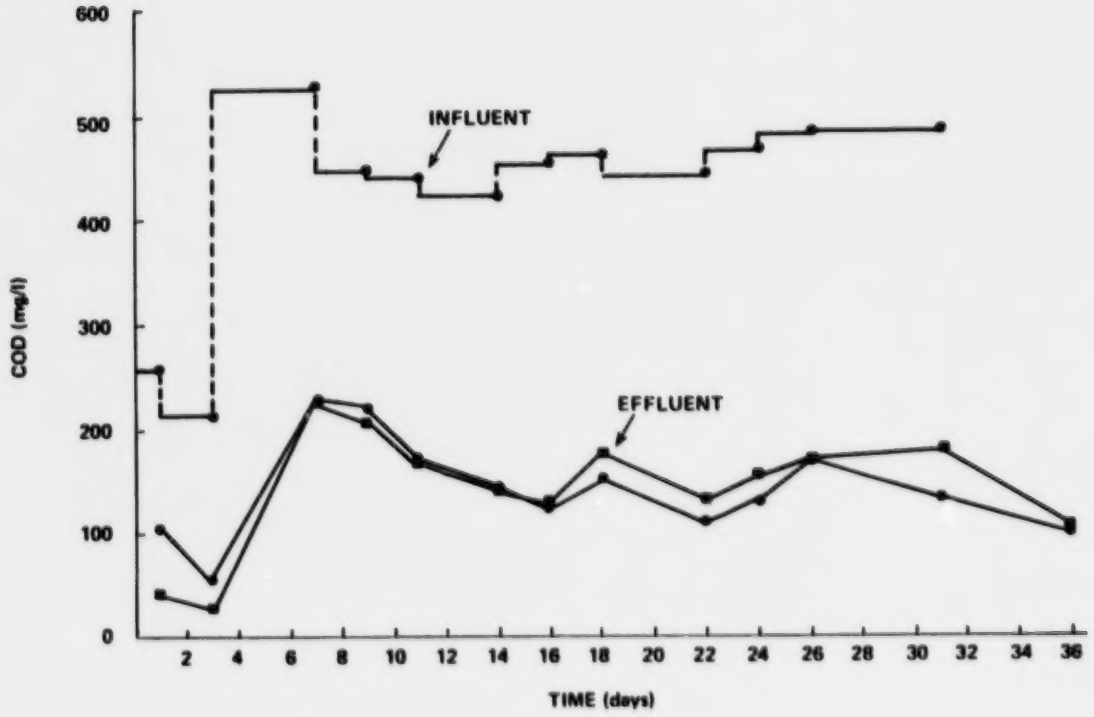


Figure 2. Influent and Effluent COD for Test Units Fed 1:100 Dazomet Wastewater.

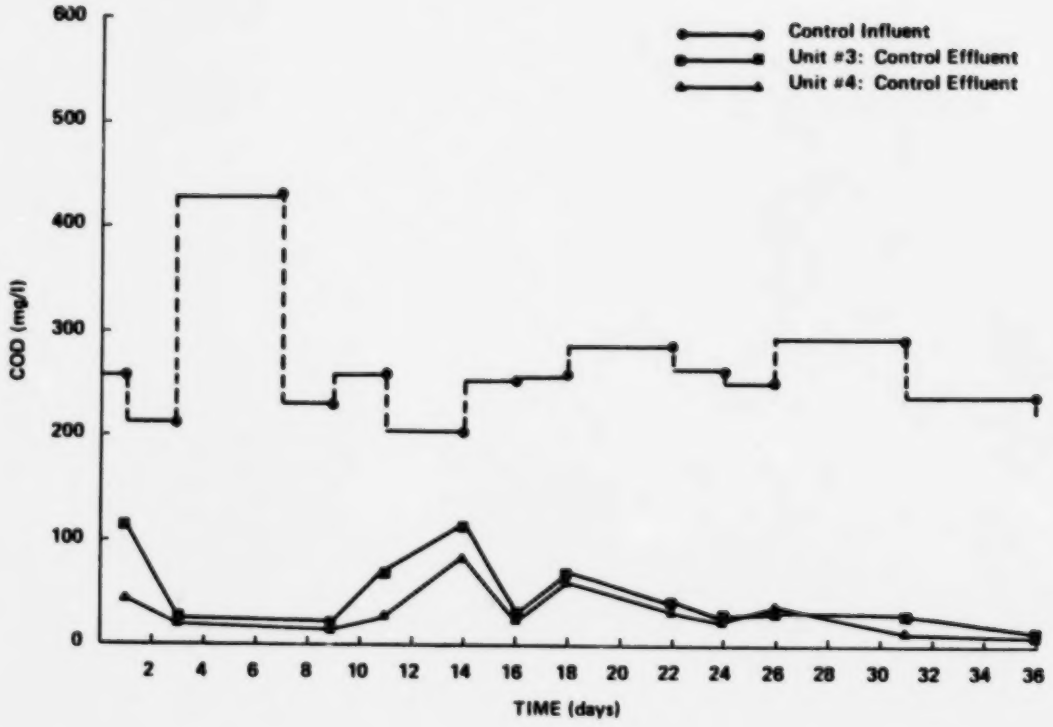


Figure 3. Influent and Effluent COD for Control Units.

pretreatment step to reduce the COD of the wastewater and the source of the nitrification inhibition. A pretreatment step involving hydrolysis and air stripping under alkaline conditions was attempted. It was hypothesized that dazomet would be fairly rapidly hydrolyzed and that several components in the wastewater together with the byproducts of this hydrolysis (ammonia, methylamine, methylisothiocyanate, and formaldehyde) would be volatilized with the resulting loss of COD and ammonia producing compounds.

The pH of a liter of dazomet of wastewater (Sample 1) was raised to 11.6 with 3.1 mL of 10 N sodium hydroxide. The solution was then bubbled vigorously with air through an aeration stone at an undetermined flow rate at room temperature. At half hour intervals aliquots were removed, adjusted to pH 7 with H_2SO_4 and analyzed for dazomet, COD, and ammonia. Table 3 presents data on these parameters for various fractions. While the breakdown of dazomet proceeded rapidly, the COD and ammonia levels were not significantly effected by this treatment. Because these components were the major concern in the treatment of the wastewater this pretreatment option was not pursued.

BIOLOGICAL TREATMENT II

After consultations with the manufacturer and officials of the local waste treatment district it was decided that further dilution of the dazomet wastewater was warranted. Based on the average flows from the manufacturing plant and the influent flow rate to the local publicly owned treatment works (POTW) it was concluded that a dilution of between 1:2000 and 1:2500 would occur if the manufacturer discharged to the POTW at his present waste production rates. It was decided to run treatability studies using 1:500 and 1:1000 dilutions to allow a margin of safety.

The dazomet wastewater (Sample 2) to the test units A was decreased from 1:100 to 1:500 after day 36 (see Figure 4). Two control units were continued with municipal wastewater feed (see Figure 5). An additional two units (test units B) which had been fed only municipal wastewater up to day 34 were fed a dilution of 1:1000 dilution of dazomet from day 34 to day 64 (Figure 6). From day 64 through 74 the dazomet wastewater concentration of test units B was increased to 1:500.

TABLE 3. DATA FOR pH TREATMENT AND AIR STRIPPING OF DAZOMET WASTEWATER (Sample 1).

Fraction	Elapsed Time (hours)	COD mg/L	Dazomet mg/L	NH_3 mg/L as N
0	0	24,200	3150	670
1	0.5	23,910	2140	
2	1.0	20,970	1860	
3	1.5	20,770	1600	
4	2.0	20,770*	1180	
5	3.0	21,750*	925	
6	7.0	21,170*	**	696
7	22.5	19,800	**	760

*Variability in COD measurements is due in part to the formation of particulate matter in the sample after pH treatment which made representative sampling for the COD measurement difficult.

**A delay in analyses due to mechanical failure of the high performance liquid chromatography (HPLC) system rendered the results unreliable.

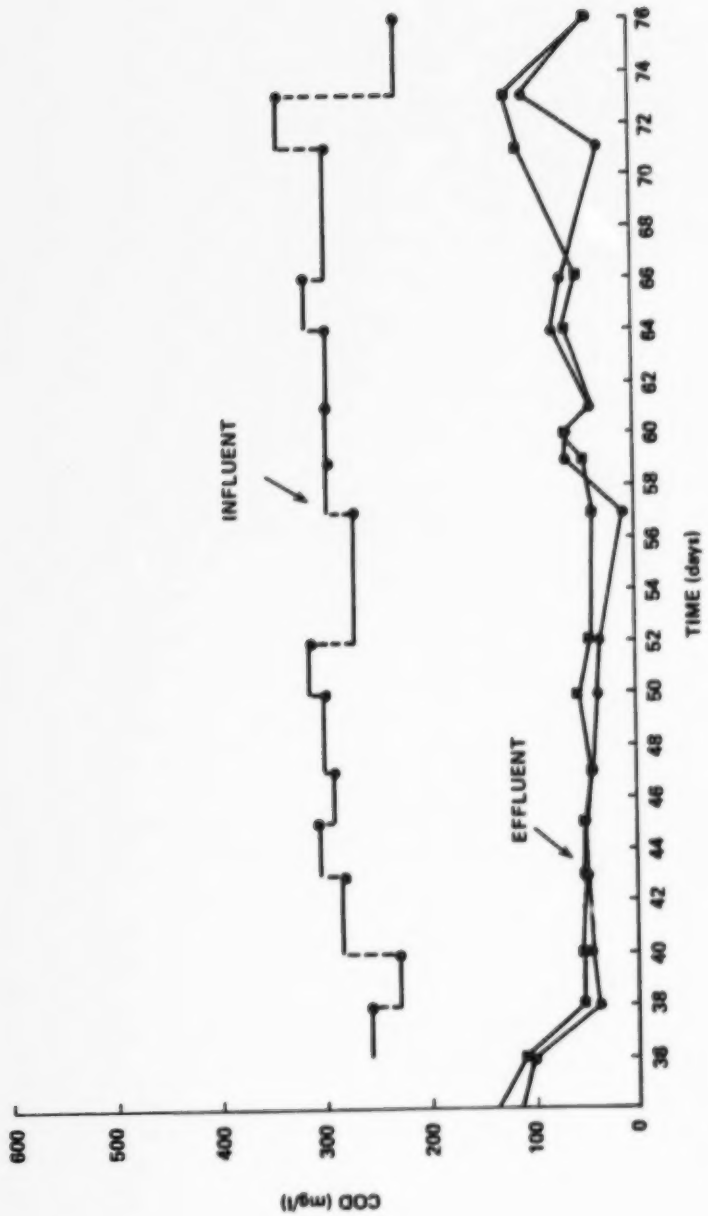


Figure 4. Influent and Effluent COD for Test Units A.

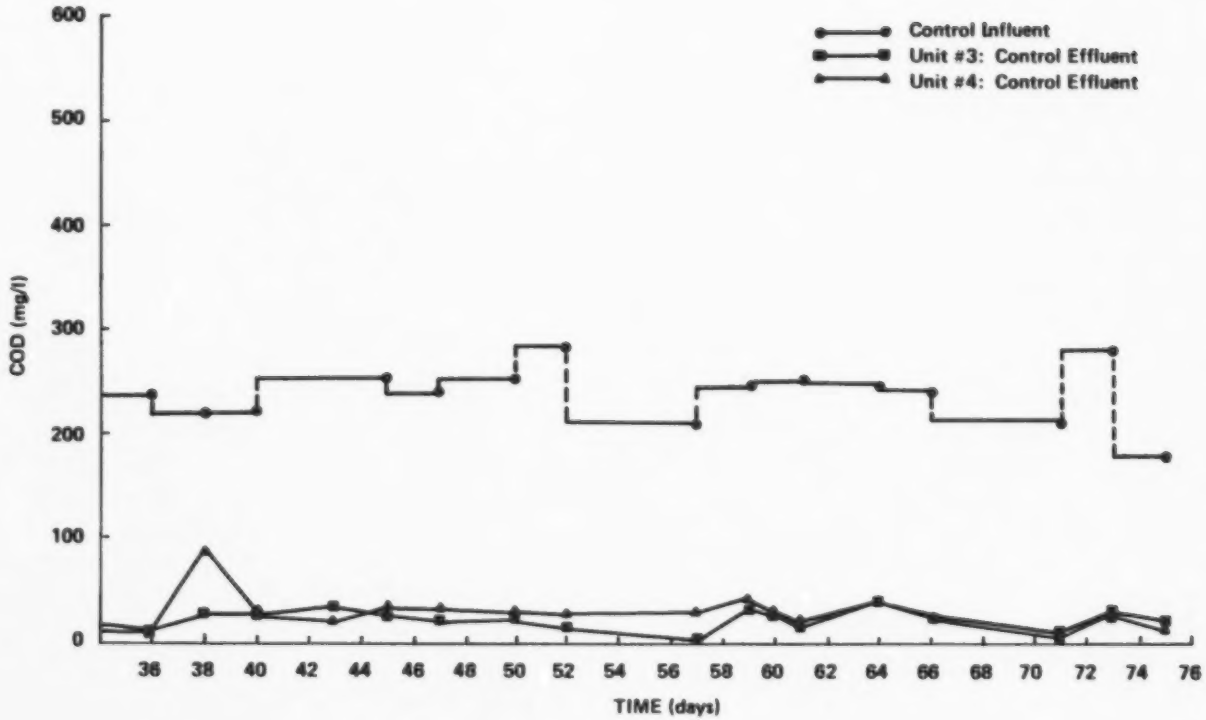


Figure 5. Influent and Effluent COD for Control Units.

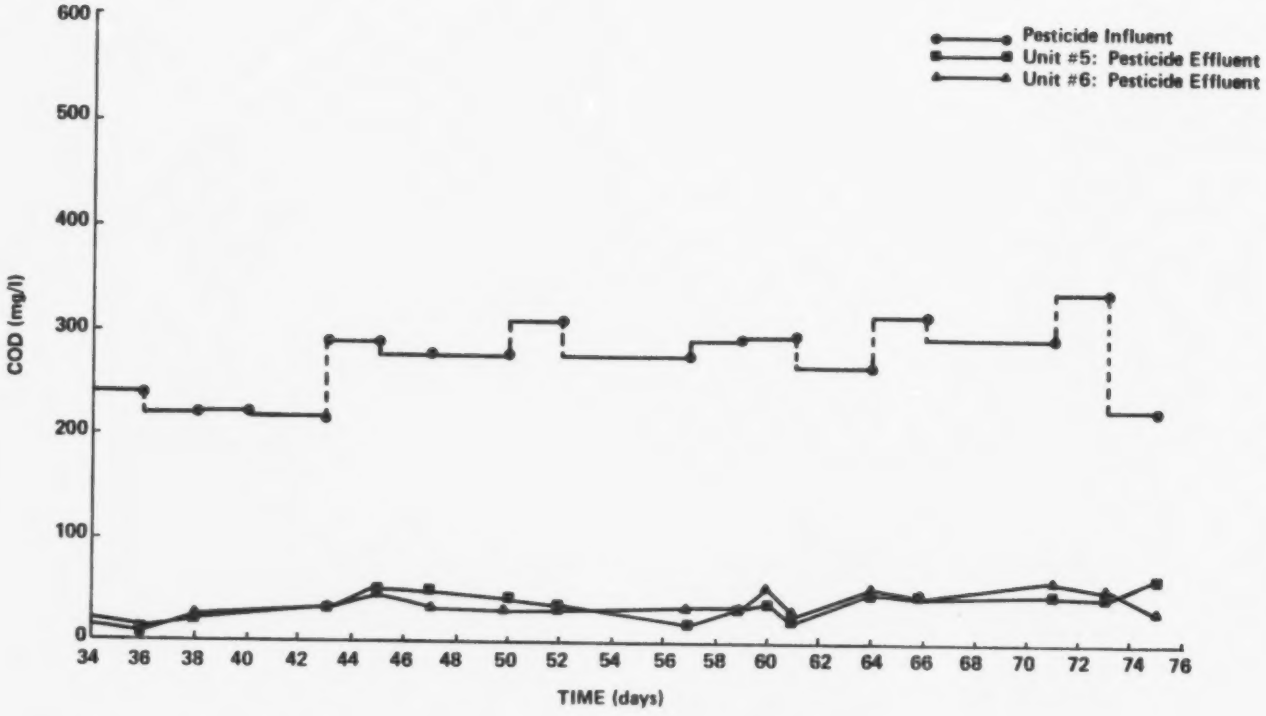


Figure 6. Influent and Effluent COD for Test Units B.

Test units B consistently performed better than test units A in terms of COD removal even during periods when both sets of units were operating at 1:500 dilutions. This performance difference may indicate that test units A never fully recovered from operating on 1% dazomet wastewater. In addition two building-wide power failures of undetermined length (up to 12 hours) on day 57 and day 63 disrupted the performance of all units. Test units A received an additional stress when the auxillary air supply used during the second failure directed an inordinately large flow of air to these units and disrupted solids settling characteristics.

Despite the increased dilution the effluent COD of test units B was significantly higher than that of the control units during the comparable period ($\tau = 10.6$, $p < 0.001$). This difference is in large part due to an increased COD removal efficiency in control units during the second four weeks of their operation as compared with the initial 4 weeks. It will be noted in Table 4 that the performance of test units B actually improved after the addition of dazomet wastewater at 1:1000 dilution though this improvement was not as great as the controls during the comparable period.

Differences were also noted in the reduction of ammonia by test and control units. The control units consistently reduced ammonia levels from 25 mg/L to 0.6 mg/L or less. Test units A continued to show inhibited nitrification. Influent ammonia levels averaged 28 mg/L and effluent levels averaged 19 mg/L. Test units B showed highly variable ammonia reduction when run on dazomet wastewaters at 1:1000 dilutions. Influent levels averaged 30 mg/L. Effluent ammonia levels averaged 7 mg/L but ranged from 1 mg/L to 16 mg/L. This variability indicates that the threshold of effect on nitrification occurs near these concentrations of dazomet wastewater. Subsequently when test units B were run on 1:500 dilutions of dazomet wastewater, the effluent ammonia levels increased to 18 mg/L.

Attempts to increase the sensitivity of the dazomet analysis in order to monitor levels in the effluent of test units A and B were

TABLE 4. COD REDUCTION IN TEST AND CONTROL UNITS.

	Day		
	4-34	34-64	64-74
Control Units			
Influent, COD, mg/L	257	242	259
Effluent, COD, mg/L	42	30	20
Reduction	84%	88%	92%
Test Units A			
Influent COD, mg/L	467	286	323
Effluent COD, mg/L	164	51	92*
Reduction	65%	82%	72%
Test Units B			
Influent COD, mg/L	257	276	323
Effluent COD, mg/L	40	36	52
Reduction	84%	87%	84%

*Units losing solids.

thwarted by the apparent decomposition of the analytical reference standard of dazomet as obtained from the Environmental Protection Agency. This decomposition was manifested in the appearance of a second and eventually larger peak in the chromatogram of the dazomet reference standard. A second reference standard was obtained but this standard showed a similar decomposition pattern on delivery which made calibration of the analytical systems impossible. Attempts to purify the dazomet standard by fractional crystallization did not separate the two compounds.

Using calibration curves from the 1:100 analyses it was determined that freshly mixed 1:500 dazomet influent contained 2.8 $\pm$ 0.1 mg/L dazomet. Influent after 24 hours contained from 1.4 to 1.9 mg/L dazomet. No dazomet was detected in any effluent samples (< 1 mg/L).

Based on the results of the decomposition of dazomet under the 1:100 dilution conditions, it would not appear that degradation of dazomet would be difficult under these conditions of increased dilution.

TOXICOLOGICAL ASSESSMENT OF DAZOMET WASTEWATER

Positive evidence for the biological treatability of dazomet wastewater was provided by the toxicological assessment of this wastewater before and after treatment. A discussion of the methods for daphnia and algal assays is provided in Appendices D and E.

Dazomet wastewater as received from the plant (Sample 2) was highly toxic to Daphnia magna and Selenastrum capricornutum. As shown in Table 5 the algal EC_{50} (concentration effective in reducing growth to 50% of controls) of settled dazomet wastewater is between 1 ml/L and 0.1 ml/L. As shown in Table 6 the 48 hour LC_{50} (concentration lethal to 50% of the daphnia population) of dazomet wastewater is between 0.1 and 0.01 ml/L.

When dazomet wastewater was diluted 1:1000 with municipal wastewater the algal EC_{50} was increased to a concentration between 320 to 1000 ml/L (see Table 7). At lower concentrations this mixture appeared to be stimulatory to algal growth. Biological treatment decreased the toxicity of this wastewater to algae. Algal growth in undiluted dazomet effluent was almost identical to that of the control flasks, while algal growth at lower concentrations of effluent was considerably higher than controls indicating a stimulatory effect from these wastewaters (see Table 8). A similar stimulatory effect was noted with effluents from control units.

TABLE 5. EFFECT OF DAZOMET WASTEWATER ON ALGAL GROWTH

Wastewater (mL/L)	10.	1	0.1	0.01	0.001
Growth (% of control on day 14)	0.2%	0.2%	88%	91%	85%

TABLE 6. EFFECT OF DAZOMET WASTEWATER ON DAPHNIA MAGNA SURVIVAL

Wastewater (mL/L)	10	1	0.1	0.01	Control
Percent Survival (48 hours)	0%	0%	0%	100%	100%

TABLE 7. EFFECT OF DAZOMET WASTEWATER DILUTED 1:1000 IN MUNICIPAL WASTEWATER ON ALGAL GROWTH

Wastewater (mL/L)	1000	320	100	10
Growth (% of control on day 14)	0.2%	83%	151%	136%

TABLE 8. EFFECT ON ALGAL GROWTH DAZOMET WASTEWATER DILUTED 1:100(IN MUNICIPAL WASTEWATER AND BIOLOGICALLY TREATED

Wastewater (mL/L)	1000	320	100	10
Growth (% of control on Day 14)	101%	112%	189%	131%

Toxicity to Daphnia magna of dazomet wastewater when diluted 1:500 and 1:1000 in municipal wastewater was measured. Undiluted municipal wastewater was not toxic to daphnia over a 48 hour period. As shown in Tables 9 and 10 when the dazomet wastewater was added to municipal wastewater at concentrations of either 2 ml/L or 1 ml/L, the 48 hour LC_{50} of these mixtures was between 320 and 560 ml/L. Biological treatment of these mixtures reduced their toxicity. The undiluted effluents from test units A, test units B, and the control units all showed no short term toxicity to daphnia.

CONCLUSIONS

The parameter which is likely to be most sensitive to the addition of dazomet wastewater is the ability of a secondary biological treatment unit to nitrify ammonia. It should be noted that the extensive nitrification in the control bench scale units reflects the rather ideal circumstances of room temperature and constant flow rate under which these units operated. Municipal waste treatment facilities rarely achieve such complete nitrification under all conditions unless design consideration is given to ammonia reduction. Dilution rates greater than 1:1000 should minimize the effects of dazomet wastewater on the nitrification rates.

Careful consideration must be given to the method for diluting and metering dazomet wastewater to a municipal waste treatment system. Since dazomet is made in batch production units with intermittent periods of no production, provision must be made for flow equalization to avoid shocks to the biological treatment systems. This may necessitate the construction of holding tanks for dazomet wastewater on site at the production facility. Once the biological treatment is acclimated, the discharge of dazomet wastewater should be continuous even during periods of no dazomet production.

If the wastewater treatment system to which dazomet wastewater is discharged does not provide flow equalization basins, then a proportional flow system may also be necessary when discharging the dazomet wastewater. Because the input to the typical municipal waste treatment plant varies greatly over a 24 hour period, the actual dilution of a constant discharge of dazomet wastewater will vary significantly. Because the system can be adversely effected by relatively small increases in dazomet concentration,

TABLE 9. EFFECT ON DAPHNIA MAGNA SURVIVAL OF DAZOMET WASTEWATER DILUTED 1:1000 IN MUNICIPAL WASTEWATER

Wastewater (mL/L)	1000	560	320	180	100	Control
Survival (48 hours)	0%	0%	100%	80%	100%	100%

TABLE 10. EFFECT ON DAPHNIA MAGNA SURVIVAL OF DAZOMET WASTEWATER DILUTED 1:500 IN MUNICIPAL WASTEWATER.

Wastewater (mL/L)	1000	560	320	180	100	Control
Survival (48 hours)	0%	40%	100%	100%	100%	100%

it will probably be necessary to proportion the discharge rate of dazomet to reflect the hydraulic loading of the waste treatment system. A crucial concern is therefore the maintenance of a constant level of dilution in addition to continuous discharge.

If the flow dilution provisions are met the toxicological impact of dazomet wastewater after municipal biological treatment should be minimal. If fact the long term impact of dazomet discharge may be one of excessive stimulation of biological growth. A phenomenon often associated with the discharge of municipal wastewater is a large increase of algal growth in receiving waters due to the increased input of the limiting nutrients either nitrogen or phosphorous. This phenomenon is assumed to be a precursor of eutrophic conditions. The dazomet wastewater contains fairly high concentrations of nitrogen in various forms. Whether the dazomet wastewater would increase the stimulatory impact of the municipal wastewater on the receiving stream would depend on whether the receiving stream was phosphorous or nitrogen limited.

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APPENDIX A

ANALYTICAL PROCEDURE FOR DETERMINATION OF DAZOMET AND METHYL ISOTHIOCYANATE

The procedure for the analysis of dazomet and methyl isothiocyanate involves the separation and quantitation of compounds by high-performance liquid chromatography (HPLC) with a reverse phase column and an ultraviolet adsorption detection system.

A modular liquid chromatographic system was used for the analyses. The basic system consisted of the following components: 2 M6000 pumps with a M 660 solvent programmer and a U 6K injector (Waters Associates), a Model SF-770 variable wavelength ultraviolet detector (Schoeffel Instruments), and a Model 1203 UV III Monitor fixed wavelength ultraviolet detector (Laboratory Data Control). A reverse phase column packed with Partisil 10 bonded with octadecyl trichlorosilane was employed.

The mobile phase, detector and wavelength, and detection limit are given in Table A-1 for the compounds analyzed in this study.

Flow rate of the mobile phase was 2.0 ml/min. Sample injection size was 10 µL. All samples were filtered through a 5.0 µ Millipore LS filter prior to direct injection on the HPLC system.

TABLE A-1. ANALYTICAL PERFORMANCE PARAMETERS FOR THE HIGH PERFORMANCE CHROMATOGRAPHIC ANALYSIS OF DAZOMET AND METHYL ISOTHIOCYANATE.

Compound	Mobile Phase (% CH_3CN in H_2O)	Detector	Detector Wavelength (nm)	Minimum Detectable Quantity (ng)	Standard Deviation
Dazomet	35%	SF-770	285	0.01	3.9% at 1.0 mg/liter
Dazomet	35%	UV III	254	0.01	4.0% at 1.0 mg/liter
Methyl isothiocyanate	25%	SF-770	237	0.02	1.8% at 2.0 mg/liter
Methyl isothiocyanate	25%	UV III	254	0.10	3.2% at 10 mg/liter

APPENDIX B

ANALYTICAL PROCEDURES FOR ROUTINE WASTEWATER CHARACTERIZATION

Routine wastewater analyses were conducted according to Standard Methods for the Examination of Water and Wastewater, 14th Edition, (APHA, AWWA, WPCF, 1975).

pH--

pH was determined electrometrically by Method 424.

Chloride--

Chloride was measured by the mercuric nitrate method (Method 408 B).

Acidity--

Acidity, as $CaCO_3$, was determined by Method 402.

Alkalinity--

Alkalinity, as $CaCO_3$, was determined by Method 403.

Nitrogen Forms--

Total Kjeldahl nitrogen was determined after digestion, according to Method 42. Ammonia (NH_3-N) was determined by an acidimetric method as described in Sections 418 A and 418 D. Nitrite and nitrate nitrogen (NO_2-N, NO_3-N) were determined by the Devarda's alloy method (419 F).

COD--

Chemical oxygen demand (COD) was determined by Method 508.

Residues--

Suspended solids (SS) were determined by Method 208 D. Total solids (TS) were determined by Method 208 A. Total dissolved solids (TDS) were determined by Method 208 A. Settleable solids were determined by Method 208 F.

APPENDIX C

PROCEDURES FOR CONDUCTING ACTIVATED SLUDGE TREATABILITY TESTS

For biological treatability studies the bench scale, complete-mix, continuous-feed, activated sludge unit designed by Swisher (1970) was employed (Figure C-1). This unit has an aerator capacity of 0.3 L and a settler capacity of 0.075 L. The unit is made entirely of glass, avoiding the possibility of contamination by organics leaching from the container. Continuous feed to the units was supplied through Teflon tubing by a peristaltic pump to give the nominal retention time of 8 hours.

The units were started with activated sludge from the Hope Valley Treatment Plant, Durham, NC , which treats municipal wastewater. The units were then fed from a reservoir of primary wastewater from the Chapel Hill Treatment Plant. When a steady-state condition was reached, as indicated by consistent effluent quality in terms of COD and mixed liquid suspended solids levels, the feed to the test units was spiked with pesticide wastewater. Control units were fed only primary wastewater.

The pesticide spiked wastewaters were prepared by adding pesticide wastewater to the primary municipal wastewater which had been allowed to settle for a 120 min to simulate primary settling. Routine determinations were made of dissolved oxygen, pH, mixed liquor volatile suspended solids in the aerator and COD, and pesticides. Dissolved oxygen was determined with an oxygen probe (Yellow Springs Instrument Co.).

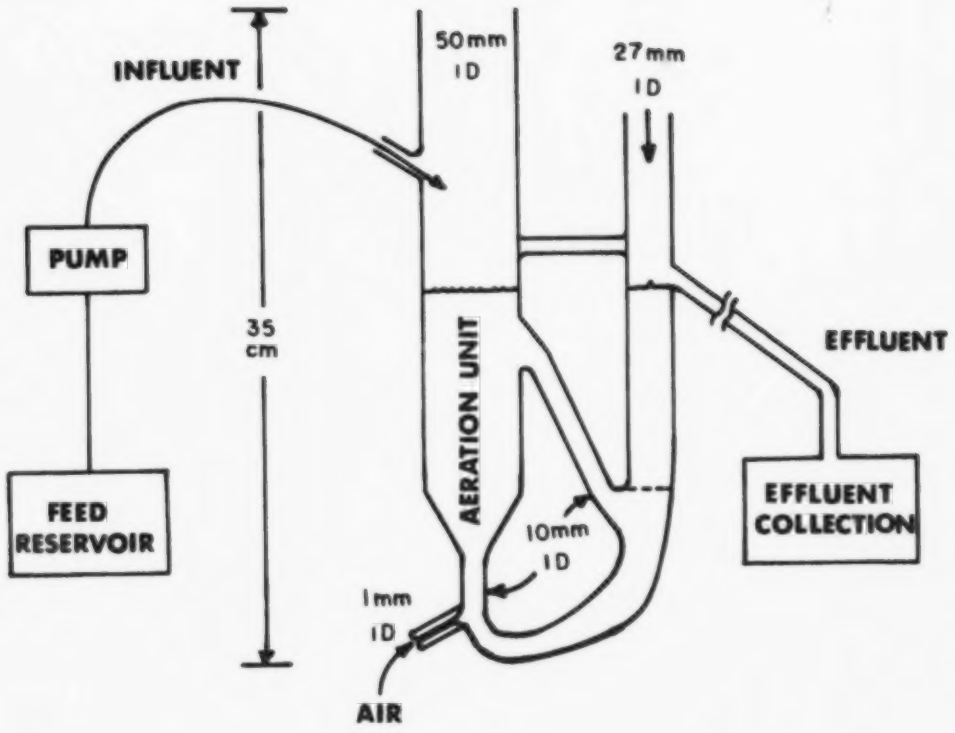

Figure C-1. Diagram of a Swisher activated sludge bench scale unit.

APPENDIX D

PROCEDURES FOR ALGAL ASSAY TESTS

Algal bioassays were conducted according to the freshwater algal assay procedure described in the report The Selenastrum Capricornutum Printz Algal Assay Bottle Test (Miller, Greene, and Shiroyama, 1978). The test alga was Selenastrum capricornutum Printz, obtained from the National Eutrophication Research Program, EPA, Corvallis, Oregon. This test was designed to measure algal response to changes in nutrient concentrations and to determine toxicity or inhibition.

Wastewaters to be tested were filter sterilized through a sterile prewashed membrane filter (Millipore Filter, 0.45 μm pore size). Serial dilutions were then made in sterile algal media to give the appropriate final concentration. Sufficient inoculum was added to produce an initial cell concentration of 10^4 cells/mL.

In each set of experiments, algal growth in the presence of a series of concentrations of the wastewater added to the nutrient medium was compared to algal growth in the nutrient medium alone. Growth was determined by direct counts of the algae during the 10-14 day incubation period. Effect of the wastewater on algal growth was determined in terms of the effect on the cell yield. Direct cell counts were performed by an automated procedure utilizing a Fisher Scientific Model FO 16 particle counter.

The tests were conducted in water bath shakers at 24 $\pm$ 2°C and at approximately 80 oscillations per minute with constant white fluorescent lighting at 4300 lux. Test containers were 250 mL Erlenmeyer Pyrex flasks containing 100 mL of test medium and covered with an inverted Pyrex beaker.

The method of expressing inhibitory or stimulatory effects was that recommended by Miller et al. (1978), i.e., as the percent growth inhibition (I) or stimulation (S), as compared to growth in a control culture without

the test materials. These authors suggest that, in general practice, the results be based on the growth at 14 days, i.e., as % I_{14} or % S_{14} at a given concentration of the effluent being tested.

Decreased growth, compared to the control, is evidence of an inhibitory effect. The manner in which the test is conducted does not allow determination of whether this inhibition is temporary (algistatic) or permanent (algicidal). Such a determination would require further testing by subculturing into fresh medium free of the test material.

APPENDIX E

PROCEDURE FOR DAPHNIA BIOASSAY TESTS

The 48 hour, static daphnia bioassay was adopted from the procedures outlined by Duke et al (1977). Daphnia magna was selected as the test species. An original population of Daphnia magna were obtained from W. T. Waller of the University of Texas at Dallas. The daphnia used in these bioassays are reared at Research Triangle Institute under conditions which promote parthenogenetic reproduction. All daphnia in the present breeding population are the offspring of a single daphnia.

Daphnia are reared in deionized water which is reconstituted to standard hard water specifications by addition of 192 mg $NaHCO_3$, 120 mg each of $CaSO_4 \cdot 2H_2O$ and $MgSO_4$ and 8 mg of KCl per liter of water. Daphnia are fed daily portions of non-sterile Selenastrum capricornutum except during testing periods.

Range finding bioassays may be conducted with a mixed population of daphnia. All narrow range, definitive bioassays are conducted with first instar young.

Tests are conducted in 250 ml beaker to which 100 mls of combined test solution and reconstituted hard water diluent are added. Ten daphnia are randomly assigned to each condition. Survival of the daphnia at 24 and 48 hours is judged by careful examination for mobility. Survival of daphnia in the control condition must be 90% or better for bioassay to be considered valid.